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ETHYLENE RANDOM COPOLYMER AND USE THEREOF

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(72) Inventor: Masaaki Kawasaki

4-9, Waki 2-chome, Waki-cho, Kuga-gun
Yamaguchi-ken

(72) Inventor: Shuji Minami

2-5, Misono 1-chome, Otake-shi
Hiroshima-ken

(72) Inventor: Hidekuni Oda

64-16, Muronoki 4-chome, Iwakuni-shi
Yamaguchi-ken

(72) Inventor: Masahiro Sugi

12-7, Shozoku-cho 5-chome, Iwakuni-shi
Yamaguchi-ken

(72) Inventor: Mikio Nakagawa

232-6, Ohno-cho, Saiki-gun, Hiroshima-ken

(71) Applicant: Mitsui Petrochemical Industries, Ltd.

2-5, Kasumigaseki 3-chome, Chiyoda-ku
Tokyo

(74) Agent: Heikichi Odajima, patent attorney and one
other

$$0.2 \leq \frac{[\text{alkenyl group}]}{[\text{5-alkenyl-2-norbornene}]} \leq 0.8 \quad (\text{II}).$$

3. Detailed Description of the Invention

[Application Field in Industry]

The present invention relates to an amorphous or low-crystalline ethylene random copolymer which exhibits excellent moldability and further relates to a use thereof.

More particularly, the present invention provides an amorphous or low-crystalline ethylene random copolymer which possesses specified structure and properties, which is excellent in melt fluidity and moldability and which can be molded into an item having excellent surface texture and luster. Furthermore, the present invention provides a thermoplastic resin modifier which is blended with a thermoplastic resin so that a composition capable of exhibiting excellent impact resistance, molding surface texture and molding luster as compared with those of the conventional amorphous or low-crystalline ethylene copolymer can be obtained without detriment to the melt fluidity and moldability.

[Prior Art]

The amorphous or low-crystalline ethylene random copolymer such as ethylene/propylene copolymer or ethylene/1-butene copolymer per se has found wide applications in soft polymer molding uses. Further, the amorphous or low-crystalline ethylene random copolymer is widely employed in the state of being either unmodified or modified by grafting an α, β -unsaturated carboxylic acid or an anhydride thereof by blending it with an olefin polymer such as polyethylene, polypropylene or poly-1-butene or a polycondensed thermoplastic resin such as a polyamide, a polyester, a polyarylene oxide, a polyacetal or a polycarbonate in order to improve the impact resistance thereof.

The known amorphous or low-crystalline ethylene random copolymers include one obtained by a copolymerization performed in the presence of a titanium based Ziegler catalyst and one obtained by a copolymerization performed in the presence of a vanadium based Ziegler catalyst. The amorphous or low-crystalline ethylene random copolymer obtained by a copolymerization performed in the presence of a titanium based Ziegler catalyst, although being excellent in melt fluidity and moldability, has a broad molecular weight distribution and

a high content of low-molecular-weight components, and produces a molded article with tacky surface even if molding is performed in unblended form or in the form of a composition. Further, the amorphous or low-crystalline ethylene random copolymer exhibits poor effect on the improvement of the impact resistance of the composition. On the other hand, the amorphous or low-crystalline ethylene random copolymer obtained by a copolymerization performed in the presence of a vanadium based Ziegler catalyst has a narrow molecular weight distribution, has a low content of low-molecular-weight components and produces a molded article with reduced surface tackiness when molding is performed in unblended form or in the form of a composition. Further, the amorphous or low-crystalline ethylene random copolymer exhibits satisfactory effect on the improvement of the impact resistance of the composition. However, the amorphous or low-crystalline ethylene random copolymer has poor melt fluidity and moldability and produces a molding with poor surface texture and luster. Therefore, in the fields of amorphous or low-crystalline ethylene random copolymer and thermoplastic resin modifier composed of the ethylene random copolymer, there is a strong demand for an ethylene random copolymer which is excellent in melt fluidity and

moldability, which produces a molded article with excellent surface texture and luster and with reduced surface tackiness and which, when used as a modifier, exhibits an excellent impact resistance enhancing effect. It is expected that the development of this ethylene random copolymer will enlarge the scope of use of the amorphous or low-crystalline ethylene random copolymer.

[Problem to be Solved by the Invention]

The inventors have found that the art of the amorphous or low-crystalline ethylene random copolymer and thermoplastic resin modifier composed of the ethylene random copolymer is in the above state and have conducted extensive and intensive investigations with a view toward developing an ethylene random copolymer which is excellent in melt fluidity and moldability, which produces a molded article with excellent surface texture and luster, and with reduced surface tackiness and which, when used as a modifier, exhibits an excellent impact resistance enhancing effect. As a result, it has been found that an ethylene random copolymer composed of an amorphous or low-crystalline ethylene/ α -olefin/5-alkenyl-2-norbornene copolymer having specified structure and properties meets the above

objects. The present invention has been completed on the basis of this finding.

According to the present invention, as an invention of product, there is provided an amorphous or low-crystalline ethylene random copolymer,

(A) comprising 40 to 96 mol% of ethylene, 60 to 4 mol% of an α -olefin having 3 to 20 carbon atoms and 0.01 to 0.7 mol% of an 5-alkenyl-2-norbornene;

(B) having an intrinsic viscosity $[\eta]$ of 0.5 to 10 dl/g as measured in 135°C decalin;

(C) having a molecular weight distribution (Mw/Mn) of 2 to 6; and

(D) having a melt flow rate measured at 230°C under a load of 2.16 kg (referred to as "MFR(2.16kg/230°C)") of 0.01 to 1000 g/10 min, the above $[\eta]$ and MFR(2.16kg/230°C) satisfying the relationship of the general formula:

$$0.80 \times [\text{MFR}(2.16\text{kg}/230^\circ\text{C})]^{-0.2} \leq [\eta] \leq 2.25 \times [\text{MFR}(2.16\text{kg}/230^\circ\text{C})]^{-0.2} \quad (\text{I}); \text{ and}$$

(E) wherein the molar ratio of double bond of alkenyl group of 5-alkenyl-2-norbornene component to 5-alkenyl-2-norbornene component of the copolymer (referred to as "[alkenyl group] / [5-alkenyl-2-norbornene]") satisfies the relationship of the general formula:

$$0.2 \leq \frac{[\text{alkenyl group}]}{[\text{5-alkenyl-2-norbornene}]} \leq 0.8 \quad (\text{II}).$$

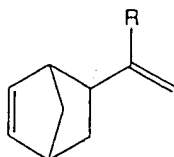
Moreover, as an invention of use, there is provided a thermoplastic resin modifier comprising the above amorphous or low-crystalline ethylene random copolymer.

In the makeup of the ethylene random copolymer of the present invention, the content of ethylene component (a) is in the range of 40 to 96 mol%, preferably 50 to 90 mol%, and still preferably 60 to 85 mol%. The content of α -olefin component (b) is in the range of 60 to 4 mol%, preferably 50 to 10 mol%, and still preferably 40 to 15 mol%. The content of 5-alkenyl-2-norbornene component (c) is in the range of 0.01 to 0.7 mol%, preferably 0.04 to 0.6 mol%, and still preferably 0.08 to 0.4 mol%. With respect to the above contents, the total of ethylene component (a), α -olefin component (b) and 5-alkenyl-2-norbornene component (c) is 100 mol%. When the content of ethylene component is less than 40 mol% and the content of α -olefin component is larger than 60 mol% in the ethylene random copolymer, the glass transition temperature of the ethylene random copolymer is increased to thereby cause the low temperature properties of the composition to become poor. When the content of ethylene component is larger than 96 mol% and the content of α -olefin component is less than 4 mol%, the crystallinity of the ethylene random copolymer is increased

to thereby cause the effect of improving the impact resistance of the composition to become poor. Further, when the content of 5-alkenyl-2-norbornene component is larger than 0.7 mol% in the ethylene random copolymer, the mechanical strength of the ethylene random copolymer is lowered. When the content of 5-alkenyl-2-norbornene component is less than 0.01 mol%, the effect of improving the melt fluidity and moldability of the ethylene random copolymer is deteriorated.

The α -olefin component of the ethylene random copolymer has 3 to 20 carbon atoms, examples of which include propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene.

The 5-alkenyl-2-norbornene component of the ethylene random copolymer is a compound represented by the general formula:



(IV)

wherein R represents a hydrogen atom or a lower alkyl group. This compound is, for example, any of 5-vinyl-2-norbornene, 5-isopropenyl-2-norbornene and 5-

isobutenyl-2-norbornene. Of these, 5-vinyl-2-norbornene is preferred.

In the ethylene random copolymer of the present invention, the molar ratio of double bond of alkenyl group of 5-alkenyl-2-norbornene component to 5-alkenyl-2-norbornene component of the copolymer (referred to as "[alkenyl group] / [5-alkenyl-2-norbornene]") satisfies the relationship of the general formula;

$$0.2 \leq \frac{[\text{alkenyl group}]}{[\text{5-alkenyl-2-norbornene}]} \leq 0.8 \quad (\text{II}).$$

Thus, the molar ration is in the range of 0.2 to 0.8, preferably, in the range of 0.3 to 0.7.

The molar ratio of alkenyl group to 5-alkenyl-2-norbornene of the ethylene random copolymer was determined by the following method.

The amount of 5-alkenyl-2-norbornene was determined from the amount consumed by the polymerization, and the amount of alkenyl group was calculated from the value determined by C^{13} -NMR.

The ethylene random copolymer of the present invention has a branched structure in which three components of the ethylene component, the α -olefin component and the 5-alkenyl-2-norbornene component are randomly arranged but has not a gel crosslink structure (three-dimensional

network crosslink structure). That the ethylene random copolymer of the present invention has not a gel crosslink structure (three-dimensional network crosslink structure) can be confirmed by the complete dissolution of the ethylene random copolymer in 135°C decalin.

The intrinsic viscosity $[\eta]$ as measured in 135°C decalin of the ethylene random copolymer of the present invention is in the range of 0.5 to 10 dl/g, preferably 0.7 to 5 dl/g, and still preferably 1 to 3 dl/g. When the intrinsic viscosity $[\eta]$ of the ethylene random copolymer is lower than 0.5 dl/g or higher than 10 dl/g, the magnificent effects of the present invention cannot be attained.

The molecular weight distribution (M_w/M_n : weight average molecular weight/number average molecular weight) as measured by gel permeation chromatography (GPC) of the ethylene random copolymer according to the present invention is in the range of 2 to 6, preferably 2 to 5, and still preferably 2 to 4. When the molecular weight distribution of the ethylene random copolymer is larger than 6, the low-molecular-weight proportion of the ethylene random copolymer is increased to such an extent that polymer tackiness becomes recognized. When the molecular weight distribution is smaller than 2, the melt fluidity and

moldability of the composition of ethylene random copolymer are lowered.

The melt flow rate measured at 230°C under a load of 2.16 kg (referred to as "MFR(2.16kg/230°C)") of the ethylene random copolymer of the present invention is in the range of 0.01 to 1000 g/10 min, preferably 0.05 to 100 g/10 min, and still preferably 0.8 to 10 g/10 min. The above intrinsic viscosity $[\eta]$ and melt flow rate MFR(2.16kg/230°C) of the ethylene random copolymer satisfy the relationship of the general formula:

$$0.80 \times [\text{MFR}(2.16\text{kg}/230^\circ\text{C})]^{-0.2} \leq [\eta] \leq 2.25 \times [\text{MFR}(2.16\text{kg}/230^\circ\text{C})]^{-0.2} \quad (\text{I}),$$

preferably

$$0.90 \times [\text{MFR}(2.16\text{kg}/230^\circ\text{C})]^{-0.2} \leq [\eta] \leq 2.0 \times [\text{MFR}(2.16\text{kg}/230^\circ\text{C})]^{-0.2}, \text{ and}$$

still preferably

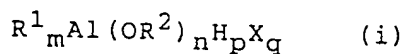
$$1.0 \times [\text{MFR}(2.16\text{kg}/230^\circ\text{C})]^{-0.2} \leq [\eta] \leq 1.75 \times [\text{MFR}(2.16\text{kg}/230^\circ\text{C})]^{-0.2}.$$

The ethylene random copolymer of the present invention is amorphous or low-crystalline. The crystallinity as measured by X-ray diffractometry of the amorphous or low-crystalline ethylene random copolymer is in the range of 0 to 50%, preferably 0 to 40%, and still preferably 0 to 30%.

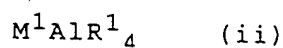
The ethylene random copolymer of the present invention can be produced by copolymerizing ethylene, an α -olefin and a 5-alkenyl-2-norbornene in a hydrocarbon medium in the presence of a catalyst composed of soluble vanadium compound catalyst component [A] and organoaluminum compound catalyst component [B]. Appropriate catalyst and polymerization conditions can be selected and employed in conformity with the following description to thereby enable obtaining the ethylene random copolymer of the present invention.

The soluble vanadium compound component used as a catalyst composing component in the copolymerization reaction consists of a vanadium compound component which is soluble in a hydrocarbon medium of the polymerization reaction system. For example, the vanadium compound component is composed of a vanadium compound of the general formula $\text{VO}(\text{OR})_a\text{X}_b$ or $\text{V}(\text{OR})_c\text{X}_d$ (wherein R represents a hydrocarbon group, $0 \leq a \leq 3$, $0 \leq b \leq 3$, $2 \leq a+b \leq 3$, $0 \leq c \leq 4$, $0 \leq d \leq 4$, and $3 \leq c+d \leq 4$) or an electron donor adduct thereof. More specifically, the vanadium compound component is composed of, for example, VOCl_3 , $\text{VO}(\text{OC}_2\text{H}_5)\text{Cl}_2$, $\text{VO}(\text{OC}_2\text{H}_5)_2\text{Cl}$, $\text{VO}(\text{O-iso-C}_3\text{H}_7)\text{Cl}_2$, $\text{VO}(\text{O-n-C}_4\text{H}_9)\text{Cl}_2$, $\text{VO}(\text{OC}_2\text{H}_5)_3$, VOBr_3 , VCl_4 , VOCl_3 , $\text{VO}(\text{O-n-C}_4\text{H}_9)_3$ and $\text{VCl}_3 \cdot 2\text{OC}_8\text{H}_{17}\text{OH}$.

A compound having at least one intramolecular Al-carbon bond can be used as the organoaluminum compound catalyst component in the copolymerization reaction. It can be, for example, an organoaluminum compound represented by the general formula:

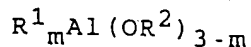


wherein each of R^1 and R^2 independently represents a hydrocarbon group generally having 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms; X represents a halogen; and m, n, p and q are numbers satisfying the relationships: $0 \leq m \leq 3$, $0 \leq n < 3$, $0 \leq p < 3$ and $0 \leq q < 3$, provided that $m + n + p + q = 3$, or a complex alkylation product of Group 1 metal and aluminum, represented by the general formula:

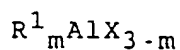


wherein M^1 represents Li, Na or K, and R^1 is as defined above.

The organoaluminum compound of the general formula (i) can be selected from among, for example, those represented by the general formula:

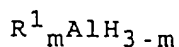


wherein R^1 and R^2 are as defined above, and m is preferably a number satisfying the relationship $1.5 \leq m \leq 3$; the general formula:



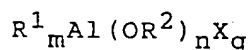
wherein R^1 is as defined above, X represents a halogen, and m preferably satisfies the relationship $0 < m < 3$;

the general formula:



wherein R^1 is as defined above, and m preferably satisfies the relationship $2 \leq m < 3$; and

the general formula:



wherein R^1 and R^2 are as defined above, X represents a halogen, $0 < m \leq 3$, $0 \leq n < 3$, $0 \leq q < 3$, and $m + n + q = 3$.

More specifically, the aluminum compound of the general formula (i) can be selected from among, for example, trialkylaluminums such as triethylaluminum and tributylaluminum; trialkylaluminums such as triisopropylaluminum; dialkylaluminum alkoxides such as diethylaluminum ethoxide and dibutylaluminum butoxide; alkylaluminum sesquialkoxides such as ethylaluminum sesquiethoxide and butylaluminum sesquibutoxide, and furthermore partially alkoxylated alkylaluminums of average composition represented by, for example, $R^1_{0.5} Al(OR^2)_{0.5}$; dialkylaluminum halides such as diethylaluminum chloride, dibutylaluminum chloride and diethylaluminum bromide; partially halogenated alkylaluminums, for example, alkylaluminum sesquihalides

such as ethylaluminum sesquichloride, butylaluminum sesquichloride and ethylaluminum sesquibromide, and alkylaluminum dihalides such as ethylaluminum dichloride, propylaluminum dichloride and butylaluminum dibromide; partially hydrogenated alkylaluminums, for example, dialkylaluminum hydrides such as diethylaluminum hydride and dibutylaluminum hydride, and alkylaluminum dihydrides such as ethylaluminum dihydride and propylaluminum dihydride; and partially alkoxyated and halogenated alkylaluminums such as ethylaluminum ethoxychloride, butylaluminum butoxychloride and ethylaluminum ethoxybromide. Moreover, use can be made of an organoaluminum compound having at least two aluminum atoms bonded with each other through an oxygen atom or a nitrogen atom as a compound similar to that of the general formula (i). This organoaluminum compound can be, for example, any of those represented by the formulae: $(C_2H_5)_2AlOAl(C_2H_5)_2$, $(C_4H_9)_2AlOAl(C_4H_9)_2$ and $(C_2H_5)_2AlNAl(C_2H_5)_2$.



The compound of the general formula (ii) is, for example, $LiAl(C_2H_5)_4$ or $LiAl(C_7H_{15})_4$. Of these compounds, preferred use is made of an alkylaluminum halide, an alkylaluminum dihalide or a mixture thereof.

The copolymerization reaction is performed in a hydrocarbon medium. The hydrocarbon medium can be selected from among, for example, aliphatic hydrocarbons

such as hexane, heptane, octane and kerosene; alicyclic hydrocarbons such as cyclohexane and methylcyclohexane; aromatic hydrocarbons such as benzene, toluene and xylene; and the aforementioned polymerizable unsaturated monomers. At least two of these hydrocarbons can be used in the form of a mixed medium.

In the process of producing the ethylene random copolymer of the present invention, the copolymerization reaction is performed in a continuous manner. In this process, the concentration of soluble vanadium compound fed into the polymerization reaction system is up to 10 times, preferably 1 to 7 times, still preferably 1 to 5 times, and optimally 1 to 3 times the concentration of soluble vanadium compound present in the polymerization reaction system. In the polymerization reaction system, the ratio of aluminum atoms to vanadium atoms (Al/V) is at least 2, preferably 2 to 50, and still preferably 3 to 20. Each of the soluble vanadium compound and the organoaluminum compound is generally diluted with the above hydrocarbon medium before being fed into the polymerization reaction system. Although the soluble vanadium compound is preferably diluted so as to fall into the above concentration range, such a procedure that formulation into an arbitrary concentration not exceeding, for example, 50

times the concentration in the polymerization reaction system is conducted before the feeding into the polymerization reaction system is employed for the organoaluminum compound.

In the copolymerization reaction, the concentration of soluble vanadium compound in the copolymerization reaction system is generally in the range of 0.01 to 5 gram atom/liter, preferably 0.05 to 3 gram atom/liter, in terms of vanadium atom.

The copolymerization reaction is performed at -50 to 100°C, preferably -30 to 80°C, and still preferably -20 to 60°C. The copolymerization reaction is generally performed in a continuous manner. When a continuous process is employed, the ethylene, α -olefin and 5-alkenyl-2-norbornene as polymer raw materials, the soluble vanadium compound component and organoaluminum compound component as catalyst components and the hydrocarbon medium are continuously introduced in the polymerization reaction system, and the polymerization reaction mixture is continuously discharged from the polymerization reaction system. The average residence time during the copolymerization reaction, although varied depending on the types of polymer raw materials, concentration of catalyst components and temperature, is generally in the

range of 5 min to 5 hr, preferably 10 min to 3 hr. The pressure during the copolymerization reaction generally exceeds 0 and is held at up to 50 kg/cm², and preferably exceeds 0 and is held at up to 20 kg/cm². According to circumstances, an inert gas such as nitrogen or argon may be caused to be present in the copolymerization reaction system. Further, an appropriate molecular weight regulator such as hydrogen can be caused to be present for regulating the molecular weight of the copolymer.

The ratio of ethylene to α -olefin fed during the copolymerization, although varied depending on polymerization conditions, is generally in the range of about 20/80 to 80/20 in terms of molar ratio. The amount of fed 5-alkenyl-2-norbornene is in the range of 0.01 to 5 mol, preferably 0.05 to 1 mol, per 100 mol of the total of ethylene and α -olefin. The amount of fed raw material olefin is controlled so that the respective proportions of components in the formed ethylene random copolymer constitute the aforementioned composition of the ethylene random copolymer in the present invention. Further, the copolymerization reaction is continued until the intrinsic viscosity of formed ethylene random copolymer reaches the aforementioned intrinsic viscosity of the ethylene random copolymer in the present invention.

The solution of formed copolymer which is obtained by the copolymerization reaction is the solution of ethylene random copolymer in the hydrocarbon medium. The concentration of ethylene random copolymer in the formed copolymer solution is generally in the range of 2.0 to 20.0% by weight, preferably 2.0 to 10.0% by weight. The ethylene random copolymer of the present invention can be obtained by treating the formed copolymer solution according to the customary procedure.

The ethylene random copolymer of the present invention can be blended with a thermoplastic resin so that the impact resistance thereof can be improved. An olefin polymer or a polycondensation resin can be mentioned as the thermoplastic resin.

Examples of suitable olefin polymers include crystalline ethylene polymers composed mainly of ethylene units, such as polyethylene, ethylene/propylene copolymer, ethylene/1-butene copolymer, ethylene/1-hexene copolymer and ethylene/4-methyl-1-pentene copolymer, and crystalline α -olefin polymers composed mainly of units of an α -olefin having at least 3 carbon atoms, such as polypropylene, poly-1-butene, poly-4-methyl-1-pentene, poly-1-hexene, propylene/ethylene copolymer and propylene/1-butene copolymer.

Examples of suitable polycondensation resins include polyesters such as polyethylene terephthalate and polybutylene terephthalate; polyamides such as polyhexamethylenedipamide, polyoctamethylenedipamide, decamethylenedipamide, dodecamethylenedipamide and polycaprolactam; polyarylene oxides such as polyphenylene oxide; polyacetals and polycarbonates.

With respect to the blending ratio, 5 to 60 parts by weight, preferably 10 to 50 parts by weight, and still preferably 10 to 40 parts by weight of the thermoplastic resin modifier of the present invention is blended with 100 parts by weight of the thermoplastic resin. According to necessity, the thermoplastic resin modifier can be blended into the thermoplastic resin in combination with various additives such as an antioxidant, a hydrochloric acid absorber, an anticoagulant, a heat stabilizer, an ultraviolet absorber, a lubricant, a weathering stabilizer, an antistatic agent, a nucleating agent, a pigment and a filler. The blending ratio of these additives can appropriately be determined.

Customary procedure can be employed in the preparation of the thermoplastic resin composition through blending of the thermoplastic resin modifier of the present invention with the thermoplastic resin.

[Example]

The present invention will be concretely illustrated below with reference to the following Examples. The measuring of the properties of the ethylene random copolymer of the present invention and the evaluation of the thermoplastic resin composition were performed by the following methods.

- (1) The makeup of the copolymer and the alkenyl group content thereof were measured by C^{13} -NMR.
- (2) The melt flow rate MFR(2.16kg/230°C) was determined in accordance with ASTM D1238.
- (3) The intrinsic viscosity $[\eta]$ was measured in decalin at 135°C.

Example 1

Terpolymerization of ethylene, propylene and 5-vinyl-2-norbornene was continuously performed with the use of a 15 liter stainless steel polymerizer equipped with an agitating blade.

From an upper part of the polymerizer, hexane, ethylene, propylene and 5-vinyl-2-norbornene were fed at respective hourly rates of 5 liter, 200 liter, 200 liter and 2.5 g. Further, hydrogen was fed so that the hydrogen concentration of the gas phase in the polymerizer was 20

respectively. The intrinsic viscosity $[\eta]$ of the ethylene random copolymer was a value therebetween.

Examples 2 to 4 and Comparative Example 1

Copolymers with different properties were obtained in the same manner as in Example 1 except that the polymerization conditions were varied.

The obtained copolymers were evaluated in the same manner as in Example 1. The polymerization conditions, copolymer properties, etc. are specified in Table 1.

Examples 5 to 7 and Comparative Example 2

Copolymers with different properties were obtained in the same manner as in Example 1 except that propylene was replaced by butene-1 and that the polymerization conditions were varied.

Example 8

20% by weight of polymer obtained in Example 1 and 80% by weight of a propylene/ethylene block copolymer whose MFR(2.16kg/230°C) and ethylene content were 25 g/min and 12 mol%, respectively were blended together by means of Henschel mixer, melt kneaded by means of a single screw

extruder (temperature set at 210°C) and injected into test pieces by means of an injection molding machine.

The properties of the test pieces were evaluated by the following methods. The results are shown in Table 2.

- (1) MFR(2.16kg/230°C) (g/10 min) was measured in accordance with ASTM D1238.
- (2) Gloss (%) was measured in accordance with ASTM D523.
- (3) Initial flexural modulus (kg/cm²) was measured in accordance with ASTM D790.
- (4) Izod impact strength (notched, kg.cm/cm) was measured in accordance with ASTM D256.
- (5) Appearance: The occurrence of flow mark over an injected square plate was visually inspected.

<Judgment>

O: flow marks were not conspicuous,

Δ: flow marks were relatively conspicuous, and

X: flow marks were conspicuous.

Comparative Examples 4 and 5

The polymers of Comparative Examples 1 and 2 were evaluated in the same manner as in Example 8. The results are shown in Table 2.

Both the polymers were inferior in respect of a balance of surface luster and low-temperature impact strength.

Example 9

The procedure of Example 8 was repeated except that the polymer of Example 1 used in Example 8 was replaced by the polymer of Example 3. The results are shown in Table 2.

Example 10

The procedure of Example 9 was repeated except that the propylene/ethylene block copolymer used in Example 9 was replaced by propylene homopolymer whose MFR(2.16kg/230°C) was 11 g/10 min. The results are shown in Table 3.

Comparative Example 6

The polymer of Comparative Example 1 was evaluated in the same manner as in Example 10. The results are shown in Table 3.

Example 11

20% by weight of polymer obtained in Example 1 was blended with propylene/ethylene random copolymer whose MFR(2.16kg/230°C) and ethylene content were 6 g/10 min and 3.3 mol%, respectively by means of Henschel mixer and formed into a film by means of a casting film forming machine

(molding temperature: 230°C). The properties of this film were evaluated by the following methods.

The results are shown in Table 4.

- (1) The haze (%) was measured in accordance with ASTM D1003.
- (2) The gloss (%) was measured in accordance with ASTM D523.
- (3) Film impact (kg.cm/cm): the impact fracture energy at punching the film with an impact head in 1 inch was measured.
- (4) The blocking strength was measured in accordance with ASTM D1893.

Comparative Example 7

The polymer of Comparative Example 2 was evaluated in the same manner as in Example 11. The results are shown in Table 4.

Table 1

	V conc.	VNB	α -olefin	ethylene/ α -olefin	H_2	yield	ethylene content	VNB content	vinyl group content	vinyl group content/ VNB content	MFR (2.16kg/ 230°C)	$[\eta]$	$[\eta]_A$	$[\eta]_B$
Ex.	mm λ	(g/hr)		(λ /hr)	(mol%)	(g/hr)	(mol%)	(mol%)	(mol%)	mol/mol	(g/10 min)	(dl/g)	(dl/g)	(dl/g)
1	0.4	3.5	propylene	200/200	20.7	293	80.4	0.25	0.13	0.52	2.15	1.18	0.69	1.80
2	0.3	0.5	"	"	4.4	255	80.3	0.04	0.02	0.50	0.60	2.3	0.89	2.33
3	0.3	1.5	"	190/200	15.5	287	80.1	0.13	0.08	0.62	0.38	1.68	0.98	2.58
4	0.45	7.0	"	200/200	25.5	246	80.5	0.52	0.29	0.56	7.80	0.95	0.53	1.39
5	0.5	0.5	butene-1	300/180	3.2	292	91.3	0.03	0.01	0.33	1.80	1.80	0.71	1.87
6	0.5	1.0	"	"	7.1	295	90.2	0.08	0.04	0.50	4.70	1.40	0.59	1.54
7	0.5	1.5	"	"	0.2	281	89.9	0.11	0.06	0.55	0.26	2.05	1.05	2.74
Comp.														
Ex. 1	0.4	0	propylene	210/180	2.8	305	80.0	0	0	-	0.37	2.71	0.98	2.56
2	0.45	0	"	210/190	10.5	294	80.0	0	0	-	5.40	1.60	0.57	1.50
3	0.6	0	butene-1	270/150	0	246	88.6	0	0	-	1.70	2.00	0.72	1.89

Catalyst: VO(OEt)Cl₃-AlEt_{1.5}Cl_{1.5}/AlEtCl₂(Al/V=8)

Polymerization temp.: 80°C

VNB: 5-vinyl-2-norbornene

$$[\eta]_A = 0.80 \times [\text{MFR}(2.16\text{kg}/230^\circ\text{C})]^{-0.2}$$

$$[\eta]_B = 2.10 \times [\text{MFR}(2.16\text{kg}/230^\circ\text{C})]^{-0.2}$$

Table 2

	Modifier	Blend ratio (wt%)	MFR(2.16kg/230°C) (g/10 min)	Gloss (%)	Initial flexural modulus (kg/cm ²)	Izod impact value (kg.cm/cm)		Appearance
						-20°C	-40°C	
Ex. 8	Ex. 1	20	16.0	79	10,000	12.2	10.1	○
9	3	20	11.5	60	10,100	21.0	13.5	○
Comp. Ex. 4	1	20	13.5	34	9,100	14.2	11.6	×
5	2	20	18.5	80	10,000	8.5	7.4	△

Table 3

	Modifier	Blend ratio (wt%)	MFR(2.16kg/230°C) (g/10 min)	Gloss (%)	Initial flexural modulus (kg/cm ²)	Izod impact value (kg.cm/cm)		Appearance
						23°C	0°C	
Ex. 10	Ex. 3	20	5.6	70	14,200	8.9	4.3	○
Comp. Ex. 6	Comp. Ex. 1	20	6.2	56	13,800	7.0	3.2	×

Table 4

	Modifier	Blend ratio (wt%)	Haze (%)	Gloss (%)	Film impact 0°C (kg.cm/cm)	Blocking strength (g/cm)
Ex. 11	Ex. 1	20	2.9	105	2200	2.4
Comp. Ex. 7	Comp. Ex. 2	20	3.5	83	1900	2.5

[Effect of the Invention]

The amorphous or low-crystalline ethylene random copolymer of the present invention is excellent in melt fluidity and moldability, produces a molded article with excellent surface texture and luster, and with reduced surface tackiness and, when used as a thermoplastic resin modifier, exhibits an excellent impact resistance enhancing effect with the result that a thermoplastic resin composition which is excellent in the above properties can be obtained.

Applicant: Mitsui Petrochemical Industries, Ltd.

Agent: Heikichi Odajima, patent attorney, and one other

⑩ 日本国特許庁(JP)

⑪ 特許出願公開

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⑮ 発明の名称 エチレン系ランダム共重合体およびその用途

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⑱ 発 明 者 川 崎 雅 昭 山口県玖珂郡和木町和木2丁目4番9号
⑱ 発 明 者 南 修 治 広島県大竹市御園1丁目2番5号
⑱ 発 明 者 小 田 秀 邦 山口県岩国市室の木町4丁目64番16号
⑱ 発 明 者 杉 正 浩 山口県岩国市莪束町5丁目12番7号
⑱ 発 明 者 中 川 幹 夫 広島県佐伯郡大野町232番地の6
⑲ 出 願 人 三井石油化学工業株式 東京都千代田区霞が関3丁目2番5号
会社
⑳ 代 理 人 弁理士 小田島 平吉 外1名

明 細 書

1 発明の名称

エチレン系ランダム共重合体およびその用途

2 特許請求の範囲

(1) (A) エチレン40ないし96モル%、

炭素原子数が3ないし20の α -オレフィン60ないし4モル%及び5-アルケニル-2-ノルボルネン0.01ないし0.7モル%の範囲からなり、

(B) 135℃でのデカリン中で測定した溶解粘度 $[\eta]$ が0.5ないし10dl/gであり、

(C) 分子量分布(M_w/M_n)が2ないし6であり、

(D) 230℃及び荷重2.16kgで測定したノルトフローレート $[MFR]_{230}^{2.16kg}$ が0.01ないし1000g/10minの範囲にあり、かつ上式(1)と $[MFR]_{230}^{2.16kg}$ とが一般式(1)

$$0.80 \times ([MFR]_{230}^{2.16kg})^{\dots} \leq [\eta] \leq$$

$$2.25 \times ([MFR]_{230}^{2.16kg})^{\dots} \quad [1]$$

の関係を充足し、

(E) 共重合体中の5-アルケニル-2-ノルボルネン成分と、5-アルケニル-2-ノルボルネンのアルケニル基に基づく二重結合のモル比が一般式(2)

$$0.2 \leq \frac{[\text{アルケニル基}]}{[\text{5-アルケニル-2-ノルボルネン}]} \leq 0.8 \quad [2]$$

である

ことを特徴とする非晶性ないし低結晶性のエチレン系ランダム共重合体。

(2) (A) エチレン40ないし96モル%、 α -オレフィン60ないし4モル%及び5-アルケニル-2-ノルボルネン0.01ないし0.7モル%の範囲からなり、

(B) 135℃でのデカリン中で測定した溶解粘度 $[\eta]$ が0.5ないし10dl/gであり、

(C) 分子量分布(M_w/M_n)が2ないし6であり、

(D) 230℃及び荷重2.16kgで測定した

共重合体からなる熱可塑性樹脂用改質剤が上記の状況にあることを認識し、熔融流動性及び成形性に優れ、成形体の収縮及びその逆に優れ、成形体表面のべたつきが少なく、かつ改質剤として用いた場合に対衝撃性の改善効果に優れたエチレン系ランダム共重合体の開発を鋭意検討した結果、特定の構造及び物性を有する非晶性ないし低結晶性のエチレン・ α -オレフィン・5-アルケニル-2-ノルボルネン共重合体からなるエチレン系ランダム共重合体が前記目的を充足することを見出し、本発明に到達した。

本発明によれば、

(A) エチレン40ないし96モル%、炭素原子数が3ないし20の α -オレフィン60ないし4モル%及び5-アルケニル-2-ノルボルネン0.01ないし0.7モル%の範囲からなり、

(B) 135℃のデカリン中で測定した屈折率 n_D^{25} が0.5ないし1.0dl/gであり、

(C) 分子量分布(M_w/M_n)が2ないし6であり、

本発明のエチレン系ランダム共重合体の組成はエチレン成分(a)の含有量が40ないし96モル%、好ましくは50ないし90モル%、とくに好ましくは60ないし85モル%の範囲にあり、 α -オレフィン成分(b)の含有量が60ないし4モル%、好ましくは50ないし10モル%、とくに好ましくは40ないし15モル%の範囲であり、5-アルケニル-2-ノルボルネン成分(c)の含有量が0.01ないし0.7モル%、好ましくは0.04ないし0.6モル%、とくに好ましくは0.08ないし0.4モル%の範囲である。ここで、エチレン成分(a)、 α -オレフィン成分及び5-アルケニル-2-ノルボルネン成分(c)の合計は100モル%である。該エチレン系ランダム共重合体において、エチレン成分の含有量が40モル%より少なくなり、 α -オレフィン成分の含有量が60モル%より多くなると、該エチレン系ランダム共重合体のガラス転移温度が高くなり、前記組成物の低温特性が劣るようになり、エチレン成分の含有量が96モル%より多くなり、 α -

(D) 230℃及び荷重2.16kgで測定したノルトフローレート[MFR] $_{230}^{2.18kg}$ が0.01ないし1000g/10minの範囲にあり、かつ上記(A)と[MFR] $_{230}^{2.18kg}$ とが一般式(I)

$$0.80 \times ([MFR]_{230}^{2.18kg})^{0.5} \leq [\eta] \leq$$

$$2.25 \times ([MFR]_{230}^{2.18kg})^{0.5} \quad (I)$$

の関係を充足し、

(E) 共重合体中の5-アルケニル-2-ノルボルネン成分と、5-アルケニル-2-ノルボルネンのアルケニル基に基づく二重結合のモル比が一般式(II)

$$0.2 \leq \frac{[\text{アルケニル基}]}{[5\text{-アルケニル-2-ノルボルネン}]} \leq 0.8 \quad (II)$$

である

ことを特徴とする非晶性ないし低結晶性のエチレン系ランダム共重合体が物質発明として提供され、該非晶性ないし低結晶性のエチレン系ランダム共重合体からなる熱可塑性樹脂用改質剤が用途発明として提供される。

オレフィン成分の含有量が4モル%より少なくなると、該エチレン系ランダム共重合体の結晶性が増加し、前記組成物の耐衝撃性の改善効果が劣るようになる。また、該エチレン系ランダム共重合体の5-アルケニル-2-ノルボルネン成分の含有量が0.7モル%より多くなると、該エチレン系ランダム共重合体の力学強度が低下するようになり、5-アルケニル-2-ノルボルネン成分の含有量が0.01モル%より少なくなると、該エチレン系ランダム共重合体の熔融流動性及び成形性の改善効果が低下するようになる。

該エチレン系ランダム共重合体を構成する α -オレフィン成分は炭素原子数が3ないし20の α -オレフィンであり、具体的にプロピレン、1-ブテン、1-ペンテン、4-メチル-1-ペンテン、1-ヘキセン、1-オクテン、1-デセン、1-ドデセン、1-テトラデセン、1-ヘキサデセン、1-オクタデセン、1-エイコセンなどを例示することができる。

該エチレン系ランダム共重合体を構成する5-

度は0ないし50%、好ましくは0ないし40%、とくに好ましくは0ないし30%の範囲である。

本発明のエチレン系ランダム共重合体は、可溶性バナジウム化合物触媒成分[A]及び有機アルミニウム化合物触媒成分[B]から形成される触媒の存在下に、炭化水素媒体中でエチレン、 α -オレフィン及び5-アルケニル-2-ノルボルネンを共重合することにより製造することができる。触媒及び重合条件については下記の記載から適宜に選択採用することにより、本発明のエチレン系ランダム共重合体を得ることができる。

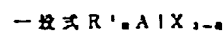
共重合反応において、触媒構成成分として使用される可溶性バナジウム化合物成分は重合反応系の炭化水素媒体に可溶性のバナジウム化合物成分であり、具体的には一般式 $VO(OR)^aX^b$ 又は $V(OR)^cXd$ (但しRは炭化水素基、 $0 \leq a \leq 3$ 、 $0 \leq b \leq 3$ 、 $2 \leq a+b \leq 3$ 、 $0 \leq c \leq 4$ 、 $0 \leq d \leq 4$ 、 $3 \leq c+d \leq 4$)で表わされるバナジウム化合物、あるいはこれらの電子供与体付加物を代表例として挙げる事ができる。より具体的には

のアルキル化合物などを挙げる事ができる。

前記の(i)に属する有機アルミニウム化合物としては、次のものを例示できる。



(ここで R^1 および R^2 は前記と同じ、 n は好ましくは $1.5 \leq n \leq 3$ の数である)。



(ここでは R^1 は前記と同じ、Xはハロゲン、 n は好ましくは $0 < n < 3$ である)。



(ここで R^1 は前記と同じ、 n は好ましくは $2 \leq n < 3$ である)。



(ここで R^1 および R^2 は前記と同じ、Xはハロゲン、 $0 < n \leq 3$ 、 $0 \leq a < 3$ 、 $0 \leq q < 3$ で、 $n+a+q=3$ である)で表わされるものを例示できる。

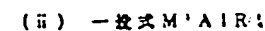
(i)に属するアルミニウム化合物において、より具体的には、トリエチルアルミニウム、トリブチルアルミニウムなどのトリアルキルアルミニウム、トリイソプロピルアルミニウムのようなトリ

$VOCl_3$ 、 $VO(OC_2H_5)Cl_2$ 、 $VO(OC_2H_5)_3$ 、 Cl 、 $VO(O-i-C_3H_7)Cl_2$ 、 $VO(O-n-C_4H_9)Cl_2$ 、 $VO(OC_2H_5)_3$ 、 $VOBr_3$ 、 VCl_3 、 $VOCl_3$ 、 $VO(O-n-C_4H_9)_3$ 、 $VCl_3 \cdot 2OC_2H_5$ 、 OH などを例示することができる。

共重合反応に使用される有機アルミニウム化合物触媒成分としては、少なくとも分子内に1個のAl-C炭素結合を有する化合物が利用でき、例えば、



(ここで R^1 および R^2 は炭素原子数通常1ないし15個、好ましくは1ないし4個を含む炭化水素基で互いに同一でも異なってもよい、Xはハロゲン、 n は $0 \leq n \leq 3$ 、 a は $0 \leq a < 3$ 、 p は $0 \leq p < 3$ 、 q は $0 \leq q < 3$ の数であって、しかも $n+a+p+q=3$ である)で表わされる有機アルミニウム化合物、



(ここで M^1 はLi、Na、Kであり、 R^1 は前記と同じ)で表わされる第1族金属とアルミニウムと

アルキルアルミニウム；ジエチルアルミニウムエトキシド、ジブチルアルミニウムブトキシドなどのジアルキルアルミニウムアルコキシド；エチルアルミニウムセスキエトキシド、ブチルアルミニウムセスキブトキシドなどのアルキルアルミニウムセスキアルコキシドのほか、 $R^1_{0.5}Al(OR^2)_{0.5}$ などで表わされる平均組成を有する部分的にアルコキシ化されたアルキルアルミニウム；ジエチルアルミニウムクロリド、ジブチルアルミニウムクロリド、ジエチルアルミニウムブロミドのようなジアルキルアルミニウムハライド；エチルアルミニウムセスキクロリド、ブチルアルミニウムセスキクロリド、エチルアルミニウムセスキブロミドのようなアルキルアルミニウムセスキハライド、エチルアルミニウムジクロリド、プロピルアルミニウムジクロリド、ブチルアルミニウムジブロミドなどのようなアルキルアルミニウムジハライドなどの部分的にハロゲン化されたアルキルアルミニウム；ジエチルアルミニウムヒドリド、ジブチルアルミニウムヒドリドなどのジアルキルアル

共重合反応は生成するエチレン系ランダム共重合体の融解粘度が前記本発明のエチレン系ランダム共重合体の融解粘度に達するまで変更される。

共重合反応によって得られる生成共重合体溶液はエチレン系ランダム共重合体の炭化水素液体溶液である。該生成共重合体溶液中に含まれるエチレン系ランダム共重合体の濃度は通常は2.0ないし20.0重量%、好ましくは2.0ないし10.0重量%の範囲にある。該生成共重合体溶液を常法に従って処理することによって本発明のエチレン系ランダム共重合体を得られる。

本発明のエチレン系ランダム共重合体は熱可塑性樹脂に配合することにより耐衝撃性を改善することができる。熱可塑性樹脂としては、オレフィン系重合体および重合体樹脂を挙げることができる。

該オレフィン系重合体として具体的には、ポリエチレン、エチレン・プロピレン共重合体、エチレン・1-ブタン共重合体、エチレン・1-ヘキセン共重合体、エチレン・4-ノルボルン-1-ペン

に好ましくは10ないし40重量部の範囲である。該熱可塑性樹脂用改質剤は必要に応じて酸化防止剤、増粘吸収剤、収束防止剤、耐熱安定剤、紫外線吸収剤、滑剤、耐熱安定剤、帯電防止剤、核剤、顔料、充填剤などの各種の添加剤と共に併用して該熱可塑性樹脂に配合することができる。これらの添加剤の配合割合は適宜である。

本発明の熱可塑性樹脂用改質剤を前記熱可塑性樹脂に配合して熱可塑性樹脂組成物を調製する方法としては、従来から公知の方法を採用することができる。

[実施例]

次に実施例によって本発明を具体的に説明する。なお、本発明のエチレン系ランダム共重合体の物性の測定及び熱可塑性樹脂組成物の評価は下記の方法に従った。

(1) 共重合体の組成およびアルケニル基含量の測定は¹³C-NMR法で行なった。

(2) ノルトフローレート[MFR]_{230°C}^{2.16kg}は、

タンなどのようにエチレンを主成分とする結晶性エチレン系重合体、ポリプロピレン、ポリ1-ブタン、ポリ4-ノルボルン-1-ペンテン、ポリ1-ヘキセン、プロピレン・エチレン共重合体、プロピレン・1-ブタン共重合体などのように炭素原子数が3以上のα-オレフィン成分を主成分とする結晶性α-オレフィン系重合体などを例示することができる。

該重合体樹脂として具体的には、ポリエチレンテレフタレート、ポリブチレンテレフタレートなどのポリエステル、ポリヘキサメチレンアジバミド、ポリオクタメチレンアジバミド、デカメチレンアジバミド、ドデカメチレンアジバミド、ポリカプロラクタムなどのポリアミド、ポリフェニレンオキシドなどのポリアリーレンオキシド、ポリアセタール、ポリカーボネートなどを例示することができる。

本発明の熱可塑性樹脂用改質剤の配合割合は該熱可塑性樹脂100重量部に対して5ないし60重量部、好ましくは10ないし50重量部、とく

ASTM D1238法により求めた。

(3) 融解粘度(η)は135℃、デカリン中で測定した。

実施例1

標準粘度を備えた15ℓのステンレス製重合器を用いて、連続的にエチレン・プロピレン・5-ビニル-2-ノルボルネンの三元共重合を行なった。

重合器上部より、毎時ヘキサンを5ℓ、エチレンを200ℓ、プロピレンを200ℓ、5-ビニル-2-ノルボルネンを2.5gの速度で、また水を重合器ガス相の水蒸気濃度が20モル%となるよう供給し、熱媒として(A)VO(OEt)Cl₂を重合器中のバナジウム原子濃度が0.4mmol/ℓとなるように、(B)Al(C₂H₅)₃・Cl₃およびAl(C₂H₅)Cl₂を重合器中のアルミニウム原子濃度がそれぞれ2.24mmol/ℓ、0.96mmol/ℓとなるように連続的に供給した。

共重合反応は60℃で行なった。

以上に述べたような条件で共重合反応を行なう

とエチレン・プロピレン・5-ビニル-2-ノルボルネン共重合体が均一な溶液状態で得られた。重合器下部から連続的に抜き出した重合溶液中に少量のメタノールを添加して重合反応を停止させ、スチームストリッピング法にて重合体を溶液から分離したのち、80℃で一昼夜減圧乾燥した。この操作でエチレン・プロピレン・5-ビニル-2-ノルボルネン共重合体が毎時256gの速度で得られた。

共重合体中のエチレン含有量は78.5mol%、極限粘度 $[\eta]$ 1.18dl/g、5-ビニル-2-ノルボルネン含量0.25mol%、ビニル含量0.13mol%であり、 $[MFR]_{230^{\circ}C}^{2.16kg}$ は2.15g/10分であった。このMFRに基づいて一般式(1)に従って計算された $[\eta]_A$ は0.69dl/g、 $[\eta]_B=1.80dl/g$ であり、このエチレン系ランダム共重合体の $[\eta]$ はこの間の値をとった。

実施例2-4 比較例1

- (2) グロス(%):ASTM D523
- (3) 白け初期弾性率(kg/cm^2):ASTM D790
- (4) アイソット衝撃強度(ノブナ付)($kg \cdot cm/cm$):ASTM D256
- (5) 外観:封出角板上のフローマークの発生の有無を目視にて観察

<判定>○:フローマークが目立たない

△:やや目立つ

×:フローマークが目立つ

比較例4,5

比較例1,2に示すポリマーを用いて、実施例8と同様の評価を行った。その結果を第2表に示す。

いずれも表面光沢、低温衝撃強度のバランスで劣る。

実施例9

実施例8で用いた実施例1のポリマーの代わりに実施例3のポリマーを用いる場合は、実施例8と同様にを行った。結果を第2表に示す。

実施例1において、種々の重合条件を変えることにより異なる性状の共重合体を得た。

得られた共重合体を実施例1と同様に評価した。重合条件、共重合体性状等を第1表に示す。

実施例5-7 比較例2

実施例1において、プロピレンをブテン-1に変えて、種々の重合条件を変えることにより異なる性状の共重合体を得た。

実施例8

実施例1で得られたポリマー:20重量%と $MFR_{230^{\circ}C}^{2.16kg}:25g/min$ 、エチレン含有率:12mol%のプロピレン・エチレンブロック共重合体:80重量%とをヘンシエルミキサーで混合後一軸押出機(設定温度:210℃)で熔融混練した後、封出成形機を用いて試験片を成形した。試験片の物性評価は以下の方法で行った。

結果を第2表に示す。

- (1) $MFR(230^{\circ}C, 2.16kg)(g/10min)$:ASTM D1238

	V 濃度 (wt%)	VNB (g/hr)	α-オレフィン	エチレン/α- オレフィン	II ₂ (wt%)	収 量 (g/hr)	エチレン 含量 (wt%)	VNB 含量 (wt%)	ビニル基 含量 (wt%)	ビニル基 含量/VNB 含量 mol/mol	MFR ^{2.16kg} _{230℃} (g/10min)	[η] (dl/g)	[η] _A (dl/g)	[η] _B (dl/g)
実施例 1	0.4	3.5	プロピレン	200/200	20.7	293	80.4	0.25	0.13	0.52	2.15	1.18	0.69	1.80
2	0.3	0.5	"	"	4.4	255	80.3	0.04	0.02	0.50	0.50	2.3	0.89	2.33
3	0.3	1.5	"	190/200	15.5	287	80.1	0.13	0.06	0.62	0.56	1.68	0.96	2.52
4	0.45	7.0	"	200/200	25.5	246	80.5	0.52	0.29	0.58	7.80	0.95	0.53	1.39
5	0.5	0.5	ブタン-1	300/180	3.2	292	91.3	0.03	0.01	0.33	1.30	1.80	0.71	1.87
6	0.5	1.0	ブタン-1	"	7.1	295	90.2	0.08	0.04	0.50	4.70	1.40	0.59	1.54
7	0.5	1.5	"	"	0.2	281	89.9	0.11	0.06	0.55	0.28	2.05	1.05	2.74
比較例 1	0.4	0	プロピレン	210/180	2.8	305	80.0	0	0	—	0.37	2.71	0.98	2.56
2	0.45	0	"	210/190	10.5	294	80.0	0	0	—	5.40	1.80	0.57	1.50
3	0.6	0	ブタン-1	270/150	0	246	88.6	0	0	—	1.70	2.00	0.72	1.89

組成: $Y_0(OEt)_2Cl_2 - AlEt_{1.5}Cl_{1.5} / AlEtCl_2 (Al/Y=8)$

混合温度: 50℃

VNB: 5-ビニル-2-ノルボルネン

$$[\eta]_A = 0.80 \times ((MFR)_{230}^{2.16kg})^{-0.1}$$

$$[\eta]_B = 2.10 \times ((MFR)_{230}^{2.16kg})^{-0.1}$$

第 2 表

外観	○	○	×	△
アイソソット融点 ($^{\circ}C$)	-40℃	10.1	13.5	7.4
	-20℃	12.2	21.0	14.2
引け初期 弾性率 (kg/cm^2)	10,000	10,100	9,100	10,000
グロス (%)	79	60	34	80
MFR ^{2.16kg} _{230℃} (g/10min)	16.0	11.5	13.5	18.5
ブレンド率 (wt%)	20	20	20	20
改質例	実施例 1	" 3	比較例 1	" 2
	実施例 3	" 5	比較例 4	" 5

実施例 10

実施例 9 で用いたプロピレン-エチレンプロポ
ク共重合体の代わりに、MFR^{2.16kg}_{230℃} : 1.1

/10 min のプロピレンホモポリマーを用いる他
は、実施例 9 と同様に行った。結果を第 3 表に示
す。

比較例 6

比較例 1 に示すポリマーを用いて、実施例 10
と同様の評価を行った。その結果を第 3 表に示す。

実施例 11

実施例 1 で得られたポリマー: 20 重量% と
MFR^{2.16kg}_{230℃} : 6 g/10 min、エチレン含有率:
3.3 mol% のプロピレン-エチレンランダム共
重合体とをヘンシニルキヤードで混合後、キヤス
トフィルム成形機(成形温度: 230℃)にてフィ
ルムを成形した。このフィルムの物性評価は以下
の方法で行った。

結果は第 4 表に示す。

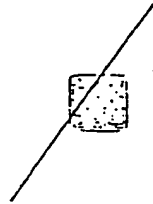
(1) ヘイズ(%): ASTM D1003

(2) グロス(%):ASTM D523

(3) フィルムインパクト($\text{kg}\cdot\text{cm}/\text{cm}$):1インチ中の衝撃面でフィルムを打ち抜く
ときの衝撃破壊エネルギーを測定する。

(4) プロツキング力:ASTM D1893

比較例7

比較例2に示すポリマーを用いて実施例11と
同様の評価を行った。その結果を第4表に示す。

第4表

	改質剤	ブレンド率 (wt%)	ヘイズ (%)	グロス (%)	フィルムインパクト 0°C($\text{kg}\cdot\text{cm}/\text{cm}$)	プロツキング力 (g/cm)
実施例11	実施例11	20	2.9	105	2200	2.4
比較例7	比較例12	20	3.5	83	1900	2.5

第3表

改質剤	ブレンド率 (wt%)	MFR $\frac{10\text{kg}}{230^\circ\text{C}}$ (g/10min)	グロス (%)	曲げ初期 弾性率 (kg/cm^2)	アイソット衝撃試験 ($\text{kg}\cdot\text{cm}/\text{cm}$)		試験
					23°C	0°C	
実施例10	20	5.6	70	14,200	8.9	4.3	○
比較例8	20	6.2	56	13,800	7.0	3.2	×

【発明の効果】

本発明の非晶性ないし低結晶性ニチレン系ラン
ダム共重合体は溶融流動性及び成形性に優れ、成
形体の収縮及びその防止に優れ、成形体表面のべたつ
きが少なく、かつ熱可塑性樹脂用改質剤として用
いた場合に耐衝撃性の改善効果に優れしかも上記
の性質に優れた熱可塑性樹脂組成物が得られる。

特許出願人 三井石油化学工業株式会社

代理人 弁護士 小田島 平 吉

外1名